NATIONAL BUREAU OF STANDARDS REPORT

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PROGRESS REPORT
ON

APATITES

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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APATITES

The term apatite refers to a structural type that can be represented by the formula $A_4B_6(MO_4)_6X_2$. In their most common forms, A and B are calcium ions in two kinds of sites, MO_4 is a PO_4, and X is OH^-, F^-, or Cl^-, but a rich variety of combinations of other elements are known to have the apatite structure. The unit-cell dimensions for the three principal apatites are given in Table 1. More complete lists are given elsewhere (1 through 5); Wondratschek (3, 4) has discussed the general characteristics of this group in some detail. The apatites, in their calcium phosphate forms, are important constituents of tooth (6), bone (7, 8), and a large number of minerals (9), and are of great commercial importance in fertilizers (11), fluorescent lamp materials (12), lasers, and chromatographic absorbents.

Fluorapatites. Most mineral apatites contain considerable fluorine, presumably because the fluoride ions suppress solubility. Fluorapatite, $Ca_{10}(PO_4)_6F_2$, may be considered to be the prototype which provides the basis for describing the structures of the other end-member apatites and their solid solutions. The space group of fluorapatite is $P6_3/m$; the unit cell contains one formula weight, $Ca_{10}(PO_4)_6F_2$; and its structure (13, 14) is shown projected on the c face in Fig. 1. The structure of fluorapatite can be visualized in three dimensions from the one given for hydroxyapatite in Fig. 2a and 2b. The origin of the unit cell was chosen to display the four groups of ions conveniently: (i) six calcium ions (Ca(II) in Fig. 2) comprising a triangular group of three on the mirror at $z = \frac{1}{4}$ and a centrosymmetrically related group on the mirror at $z = \frac{3}{4}$; (ii) two sets of three

PO_4 groups similarly arranged on the mirrors at z = $\frac{1}{4}$ and $\frac{3}{4}$; (iii) two pairs of calcium ions (Ca(I) in Fig. 2) at z = 0 and $\frac{1}{2}$, one such pair being on each of the triads near the acute corners of the cells in Fig. 1 and 2, and (iv) two fluoride ions at the centers of the Ca(II) triangles. The fluorine positions are slightly above those of the hydroxyl oxygen atoms shown in Fig. 2b.

Hydroxyapatite. Tooth and bone crystallites and some minerals, although they contain many impurity substituents, approach hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, in their compositions. It is immediately obvious that hydroxyapatite cannot truly fulfill the requirements of space group $P6_3/m$ except in a statistical sense because the symmetry of the OH^- group is less than that of the F^- ion site in fluorapatite. A substantial step in understanding the chemical and physical properties of hydroxyapatite was made when it was discovered (13, 15, 16) that the OH^- oxygens of hydroxyapatite lie about 0.37 Å above or below the planes at z = $\frac{1}{4}$ and $\frac{3}{4}$ which in fluorapatite are mirrors. This introduces possible variability in structure-dependent properties resulting from (i) differences in the ordering of OH^- groups along a given column in which the orientation of the groups may reverse at vacancies or at sites containing impurities such as F^- or O^{2-}, and (ii) polar interactions between adjacent ordered columns, which could lower the symmetry to monoclinic in micro-regions of the crystal.

These features could have significant effects on the thermodynamic properties (including solubility) of apatites and the physiological properties of tooth and bones. For example, a polar character imparted to bone crystallites by a predominant orientation of the OH^- columns in one direction along c could have important effects on the organization and properties of bone.

Chlorapatite. $Ca_{10}(PO_4)_6Cl_2$, the third principal calcium-phosphate apatite, occurs in two forms. It is monoclinic, $P2_1b$, below about 200°C, where it transforms into an apparently hexagonal phase (17, 18). Because of the nearly hexagonal symmetry of the monoclinic crystal, it shows prominent twinning (18). When heated to about 1,000°C chlorapatite tends to lose $CaCl_2$, thereby lowering the transition temperature (18).

The existence of two forms and the variability in transition temperature have been explained on the basis of the following structural considerations (16, 17). The positions of the Ca^{2+} and PO_4^{3-} ions in chlorapatite are approximately the same as those in hydroxyapatite and fluorapatite. In comparison to fluorapatite where the F^- ions are on the mirror planes at $z = \frac{1}{4}, \frac{3}{4}$, the Cl^- ions in chlorapatite are at $z = 0.44$, or about 1.27 Å away from the mirror. Thus, a given Cl^- will be closer to the calcium ions on one mirror than it is to those on the other. As a result, the greater attractive forces will bring the Ca^{2+} ion in the nearer triangle closer together than they are in the triangle slightly farther away. This difference in the Ca^{2+} triangles causes slight tilting of the PO_4^{3-} groups, thus destroying the mirror on which these ions lie in fluorapatite. These displacements are propagated from one Cl^- column to the next, thereby converting the mirror plane in fluorapatite into a glide plane in chlorapatite. When the temperature is sufficiently high, thermal motion or disorder in the Cl^- positions apparently removes the ordering in the Cl^- positions, thus producing the hexagonal form. Vacancies in the Cl^- positions are thought to have a similar effect, thereby lowering the transition temperature.

Infrared & Raman Spectra

Infrared spectra of apatites have been studied extensively (19 through 25). The bands in the spectra of powder samples have been assigned (19) with considerable reliability on the basis of (i) correlations between the spectral frequencies of calcium, strontium, and barium hydroxyapatites, fluorapatite, and hydroxyapatite-fluorapatite solid solution, (ii) isotopic shifts produced by ^{8}H and ^{18}O, (iii) comparisons with other phosphates, and (iv) various theoretical considerations such as site symmetry. These assignments (19) for hydroxyapatite are given in Table 2. The hydrogen stretching band, 3572 cm^{-1}, and librational bands, 630 cm^{-1}, are of special interest because (i) they are missing, as one would expect, in fluorapatite, (ii) they break up into several bands in fluorapatite-hydroxyapatite solid solutions in a manner one would expect if weak hydrogen bonds are formed between the OH^- and F^- ions on the hexads, and (iii) they are sensitive to the presence of impurities in the crystal, to the extent that they are missing in the spectra of bone, enamel, many mineral hydroxyapatites, and synthetic preparations containing Cl^- and CO_3^{2-}. The band at 474 cm^{-1} was particularly difficult to assign, but now appears reliably attributed to a ν_2 mode of the PO_4 group (19).

Polarized infrared and Raman spectral studies of single crystals have separated the peaks found in the spectrum of fluorapatite powders into a larger number of peaks which depend on the orientations of the beam and the plane of polarization relative to the crystal axes. Factor-group analysis (20), based on the unit-cell contents and the space-group symmetry of fluorapatite, has provided an internally consistent assignment of specific symmetries to the observed peaks. Thus although the structures of the apatites and their

infrared and Raman spectra are relatively complex, the state of understanding of these spectra are at a relatively high level.

Carbonate-containing apatites. Mineralogical and synthetic apatites can be divided generally into two classes, high-temperature (non-aqueous) and low-temperature (precipitated) products. (9, 26 through 30). Carbonate is ubiquitous in both types of apatites, but appears to be differently situated in them. The carbonate-containing mineral apatites are further subdivided into those relatively low in fluorine (dahllite) and those high in fluorine (francolite). The mineral francolite frequently contains more F^- than the 3.77% found in stoichiometric FAp (26). The presence of CO_3 is easily detected by characteristic peaks in the infrared spectra, those for the high-temperature apatites being distinct from those of the low-temperature apatites (27, 28).

In both types of apatites, the CO_3^{2-} ions are thought to be in specific sites within the apatite structure because the unit-cell dimensions, the optical properties, and the content of phosphate and various other ions (coupled substitutions) appear to vary more or less monotonically with carbonate content. It is generally held (i) that in most low-temperature apatites, the CO_3^{2-} occupies mostly the sites of PO_4^{3-} ions, the smaller size of the CO_3^{2-} ion accounting for the observed shrinkage in the a axis, and (ii) that in most high-temperature apatites the CO_3^{2-} ion is in the vicinity of the sixfold axis, where it replaces two OH^- ions; here its large size compared to two OH^- ions is thought to cause the increase in a dimension found in high-temperature carbonate apatites. Many other proposals have been put forth to explain the carbonate-apatite problem—presence of extraneous phases, adsorption on internal and external surfaces, various

sites for the CO_3^{2-} group—which may still have partial validity, but most of the present emphasis is on these two models even though unambiguous structural proof for either is lacking.

It has been reported (31) that as much as 22% CO_3 (about 3 CO_3^{2-} ions per unit cell) can be incorporated into the structure of carbonate-hydroxyapatite, and that the unit-cell dimensions change linearly with CO_3 content in this range of compositions, with a decreasing about 0.006 Å and c increasing about 0.0045 Å, respectively, for each 1% increase in CO_3 content. These variations in unit-cell dimensions are quite graphic, but it remains to be known how the loss of negative charge is compensated, and it seems incredible that the apatite structure can be maintained when three of the six PO_4^{3-} ions per unit cell are replaced by CO_3^{2-} ions.

Dry CO_2 at 900°C is taken up by hydroxyapatite to produce a material with an expanded a axis and with an infrared absorption spectrum characteristic of high-temperature carbonate apatite. The CO_3^{2-} ion is thought to lie on the sixfold axis with its plane making an angle <27° with the c axis (27, 29). In contrast to this, when fluorapatite is heated with CaO and dry CO_2, the product has a shortened a axis and the infrared absorption spectrum characteristic of low-temperature apatites in which the CO_3^{2-} is thought to be in the PO_4^{3-} site (27, 32, 33). Dichroic ratios derived from polarized infrared absorption data (27,29) suggest that the plane of the CO_3^{2-} makes an angle of 37° with the (00·1) face of the crystal; this is in accord (i) with earlier calculations (27, 29) based on birefringence measurements and, (ii) with a proposed model (34) in which the CO_3^{2-} ion occupies one of the two "sloping" faces of the PO_4^{3-} site.

Water in apatites. Stoichiometric hydroxyapatite contains constitutional water in the form of OH^- ions; this water can be driven off at high temperatures (circa 1200°C), first producing a partially dehydrated hydroxyapatite (35 through 39) (which presumably contains one O^{2-} ion for each water molecule that has been lost, and then disproportionating according to the overall reaction (40)

$$Ca_{10}(PO_4)_6(OH)_2 = Ca_4O(PO_4)_2 + 2Ca_3(PO_4)_2 + H_2O.$$

A large variety of proposals have coupled the presence of water protons, and extra hydroxyl ions with observed deviations from the ideal stoichiometry of apatites. These proposals include H_2O in place of OH^- (41), H_2O or H_3O^+ in place of Ca^{2+} (8, 42), water as $(CO_3 + H_2O)^{2-}$ substituting for PO_4^{3-} (9), $(H_4O_4)^{4-}$ in place of PO_4^{3-} (43), interstitial H^+ (as hydrogen bonds between PO_4^{3-} oxygens) (44 through 50), and water of hydration in octacalcium phosphate interlayered with hydroxyapatite (51, 52). Water may be present also in the form of acidic or hydrated calcium phosphates present as separate phases. In addition, there is NMR evidence (53, 54) for the presence of "liquid" water, which is supported by the observation that enamel crystals explode when heated (55). The infrared spectra of nearly all hydroxyapatite precipitates show the presence of strong bands in the hydrogen stretching region. The a dimension of synthetic hydroxyapatite usually decreases about 0.01 Å and the indexes of refraction increase (from about 1.630 to 1.645) when synthetic hydroxyapatite is heated. These are all indications that water is within the crystal in some form, but it is not necessarily there as H^+, H_2O, or H_3O^+ substituents in specific crystallographic sites.

Non-stoichiometry of apatites. A long-time, somewhat-controversial problem in apatite chemistry has related to the large variations in Ca/P ratios in products which otherwise appear to be pure hydroxyapatite (42, 56, 57). Many proposals have been put forth (57, 58) to account for this phenomenon, but the finely-divided state of most hydroxyapatite preparations has prevented an assessment of these proposals in the vast majority of the materials that have been studied for this purpose. Adsorption of calcium or phosphate ions is undoubtedly an important factor in many very finely-divided apatites. The presence of secondary phases (e.g., $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, $CaCO_3$) can sometimes be demonstrated by microscopic methods even when X-ray diffraction patterns do not indicate their presence. Intracrystalline mixtures of hydroxyapatite and octacalcium phosphate have been shown to occur in some instances by X-ray diffraction and optical studies of individual crystals. It is widely held (44 through 48, 50, 59), however, that low Ca/P ratios also result from the presence of calcium vacancies with charge compensation achieved by incorporation of protons interstitially, as H_3O^+ ions, or by protonating OH^- ions to form H_2O. It has been suggested (43), also, that high Ca/P ratios may result from the substitution of $(OH)_4^{4-}$ for PO_4^{3-}. Although definitive evidence for these mechanisms is lacking, it is possible that under highly irreversible conditions of precipitation, appreciable concentrations of vacancies, interstitial ions and substituents may become frozen into the structure.

Octacalcium phosphate. Although the formula of this compound, $Ca_8H_2(PO_4)_6 \cdot 5H_2O$, and its symmetry, $P\bar{1}$, differs drastically from those of hydroxyapatite, it contains a layer in which the structure resembles very closely that of hydroxyapatite (51, 60). Thus, the two salts can occur as intracrystalline,

interlayered mixtures as depicted in Fig. 3. This compatibility of the two structures introduces complexities into the chemistry of hydroxyapatite and gives insight into possible causes for some of its anomalous behavior. The platy nature of tooth and bone crystallites, which is not consistent with hexagonal symmetry, may relate to octacalcium phosphate having been a precursor during nucleation and growth (58, 61). This is in accord with the low Ca/P ratios of early tooth and bone mineral (62), and the concomitant tendency to form pyrophosphate when heated (63, 64). The conversion of octacalcium phosphate to an apatite (as well as the conversion of hydroxyapatite to fluorapatite) may be related to why fluoride in the drinking water during the first few years of life reduces dental caries (58). At least some of the apparent non-stoichiometry of hydroxyapatite must be attributed to the presence of octacalcium phosphate, either as an interlayered mixture or as intercrystalline mixture (52).

Solubility. The solubility of hydroxyapatite in the ternary system, $Ca(OH)_2$-H_3PO_4-H_2O, has been measured at four temperatures in the range 5° to 37°C (65 to 67). The solubility, in terms of the ion activity product, $(Ca^{2+})^{10}(PO_4^{3-})^6(OH^-)^2$, and derived thermodynamic quantities are listed in Tables 3 and 4. These quantities were calculated taking into account the presence of ion pairs of $CaHPO_4^\circ$ and $CaH_2PO_4^+$ (68). The stability range of hydroxyapatite is very broad. In the ternary system at 25°C, hydroxyapatite is the stable phase from pH 4.3 (below which $CaHPO_4$ is more stable) to above pH 12. However, the lower limit of the stability is not the same for all solutions. The presence of other calcium salts in the solution will generally extend the range of stability to values below 4.3,

and the presence of other phosphate salts will restrict the range to values of pH higher than 4.3 as long as $CaHPO_4$ is the other salt limiting the stability of hydroxyapatite. Very low concentrations of F^- ion in solution cause hydroxyapatite to be unstable relative to fluorapatite.

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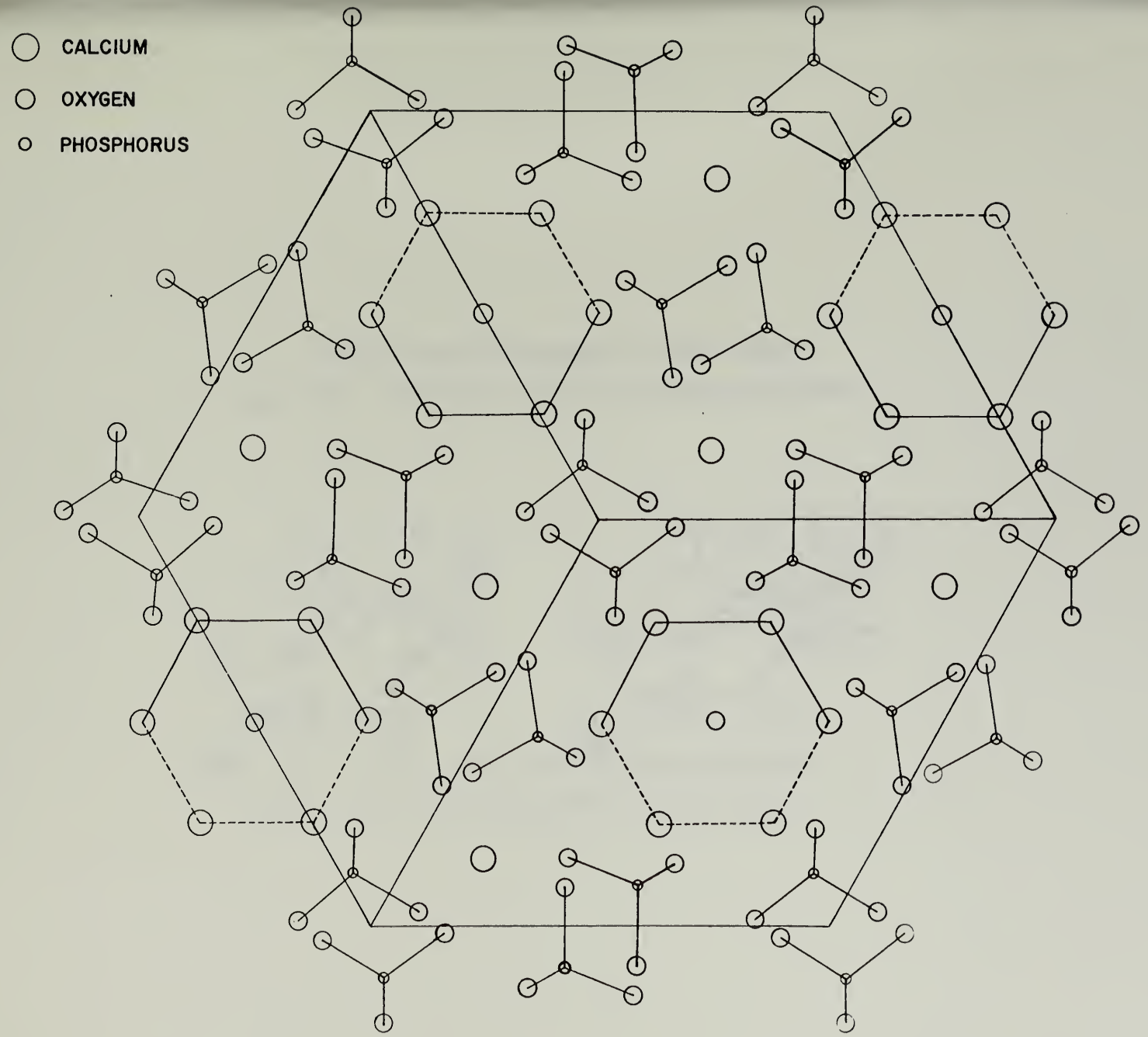

Fig. 1. Crystal structure of fluorapatite projected on 00·1.

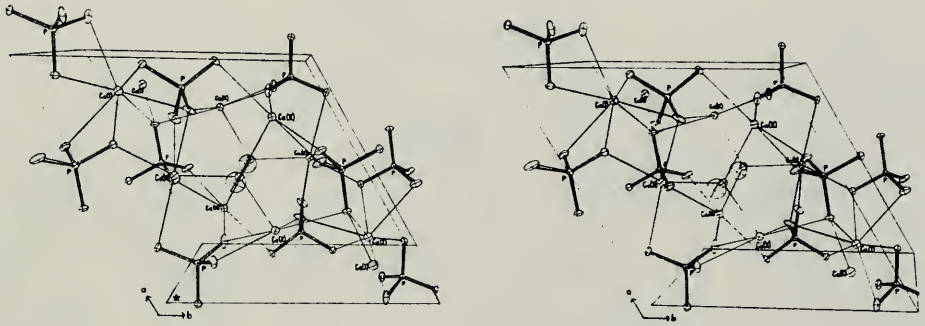

Fig. 2a. Crystal structure of hydroxyapatite viewed nearly parallel to the c axis.

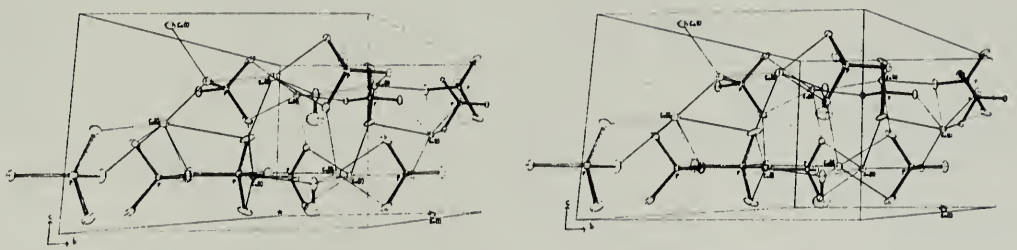

Fig. 2b. Crystal structure of hydroxyapatite viewed nearly perpendicular to the c axis.

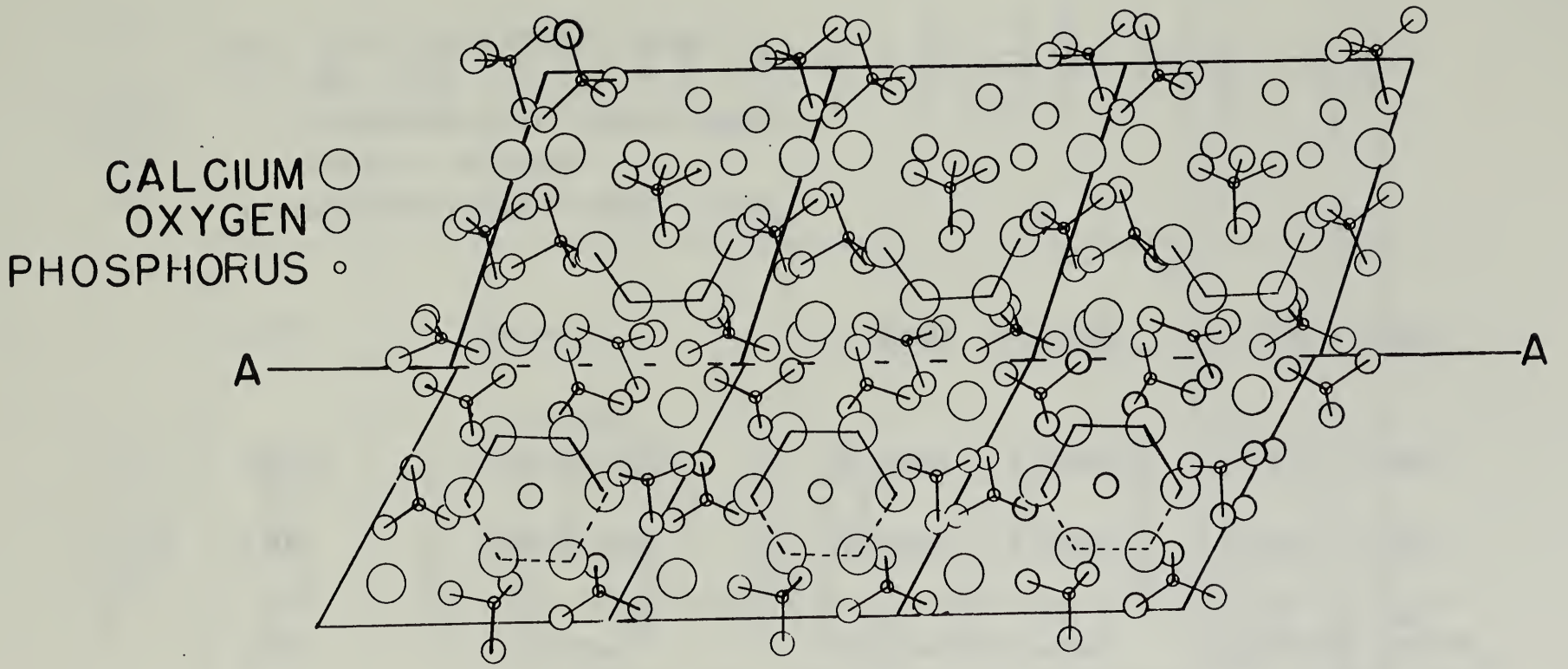

Fig. 3. The structure of octacalcium phosphate (three half unit cells are shown) and hydroxyapatite (three full unit cells) projected on the 00·1. The plane A—A is common to the two structures.

Table 1. Characterization of specimens

Type	Origin	Lattice parameters a	c	Refractive indices† n_ω	n_ϵ
FAp	Auburn, Me.	9.365(5)	6.880(5)//	1.632	1.629
OHAp*	Holly Springs, Georgia	9.424(5)	6.879(5)‡	1.650	1.646
ClAp	Synthetic	9.634(5)	6.783(5)**	1.669	1.668

* Principal known impurity, 0.3%F‡.

† YOUNG *et al* (1968).

‡ SUDARSANAN and YOUNG (1969).

// This work.

** YOUNG and ELLIOTT (1966).

Table 2. Infrared frequencies (cm^{-1}) at 48°C and assignments for calcium-, strontium-, and barium-hydroxyapatite

Ca-OHAp	Band Assignments
3572 w	OH stretch
1087 s ~ 1072 sh 1046 vs ~ 1032 sh	$\nu_3(PO_4)$ PO stretchings
962 w	$\nu_1(PO_4)$ PO symmetric stretch
630 m	OH libration
603 m 572 m	$\nu_4(PO_4)$ OPO bendings
474 w ~ 462 sh	$\nu_2(PO_4)$ OPO bendings
~ 360 sh 343 m	OH translation
~ 290 ~ 275 } m ~ 228	Cation-PO_4 lattice modes

s = strong
m = medium
w = weak
v = very
b = broad
sh = shoulder

Table 3. Standard heats, entropies and free energies of formation at 25°C*

Compound	ΔH_f° kcal/mol	ΔS_f° cal/mol deg	ΔG_f° kcal/mol	K_{sp}(calc)
$CaHPO_4$	-435.2 ±0.5	-113. ± 0.5	-401.5 ± 0.5	$2 \pm 2 \times 10^{-6}$
$CaHPO_4 \cdot 2H_2O$	-576.0 ± 0.5	-206. ± 0.5	-514.6 ± 0.5	$3 \pm 3 \times 10^{-6}$
β-$Ca_3(PO_4)_2$	-988.9 ± 1.0	-190.7 ± 0.38	-932.0 ± 1.0	$6 \pm 10 \times 10^{-34}$
$Ca_{10}(PO_4)_6(OH)_2$	-3,228.8 ± 4.0	-644.8 ± 0.2	-3,036.6 ± 4.0	
$Ca_{10}(PO_4)_6F_2$	-3,295.7 ± 4.0	-614.2 ± 0.2	-3,112.6 ± 4.0	

* Thermodynamic quantities were calculated from data compiled by ROSSINI *et al.* (1952) (67).

Table 4. Solubility product constants and thermodynamic quantities at 25°C

Compound	K_{sp}(sol)*	ΔH_f° kcal/mol	ΔS_f° cal/mol deg	ΔG_f° kcal/mol
$CaHPO_4$	$1.27 \pm 0.03 \times 10^{-7}$	-433.86 ± 0.03	-106.76 ± 0.13	-402.03 ± 0.04
$CaHPO_4 \cdot 2H_2O$	$2.59 \pm 0.04 \times 10^{-7}$	-574.46 ± 0.03	-199.52 ± 0.10	-514.97 ± 0.04
$Ca_8H_2(PO_4)_6 \cdot 5H_2O$	$1.1 \pm 1.0 \times 10^{-94}$	(-3177)	(-824)	(-2931)
β-$Ca_3(PO_4)_2$	$1.38 \pm 0.15 \times 10^{-29}$	-979.59 ± 0.14	-189.10 ± 0.38	-923.21 ± 0.18
$Ca_{10}(PO_4)_6(OH)_2$	$1.39 \pm 0.36 \times 10^{-115}$	-3206.5 ± 0.16	-640.1 ± 0.2	-3015.5 ± 0.18
$Ca_{10}(PO_4)_6F_2$	---	---	-609.4 ± 0.2	---

* Values calculated from solubility measurements allowing for formation of ion pairs. The thermodynamic quantities were calculated using revised values for aqueous ions and elements, WAGMAN *et al.* (1968, 1969).


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